Palladation of diimidazolium salts at the C4 position: access to remarkably electron-rich palladium(II) centers†

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Palladation of C2-protected diimidazolium salts with $Pd(OAc)_2$ afforded complexes comprising C4-bound N-heterocyclic dicarbene ligands. The reactivity of these complexes towards Lewis acids ($AgBF_4$, AgOAc) and Brønsted acids (H_2SO_4, H_3PO_4, HOAc) revealed that abnormal C4 bonding of the carbenes markedly increases the nucleophilicity of the coordinated palladium center as compared to C2 bonding. Despite its formal +2 charge, the palladium center in these complexes is best described as a Lewis base. The abnormal carbene bonding mode induces new reaction patterns such as the formation of a Pd–Ag adduct. Based on metallation studies including the palladation of a dissymmetric diimidazolium salt, a rationale for the selective activation of the C4–H bond in the diimidazolium precursor salts is proposed.

Introduction

The organometallic chemistry of N-heterocyclic carbenes (NHCs)[1] has provided an entirely new twist on the development of active catalysts[2] and materials for optical and electronic applications.[3] The success of NHCs in these areas is quite generally ascribed to the relative[4] stability of the $M–C_{NHC}$ bond and the strong donor ability of this type of ligand. While most studies have focused on NHC ligands resulting from metallation of imidazolium and related salts at the C2 position (**A**, Fig. 1), a variety of new NHC systems have recently been developed in which the carbene and at least one of the stabilizing heteroatoms are mutually more remote.[5] In such a ligand framework, the inductive and mesomeric influence of the heteroatom is significantly altered. As a consequence and also due to the associated steric differences, the bonding of these less stabilized carbene ligands to the metal, and likewise the reactivity patterns of the coordinated metal center vary distinctly from those of the classical imidazolium-derived NHC systems **A**.

Stimulated by its serendipitous discovery,[6] we have become interested in exploiting the potential of abnormal imidazolylidenes **B** (E = NR, Fig. 1) as ligands to transition metals.[7] Different rational procedures for installing the metal at the imidazolium C4 position have been developed in the last few years,[8] including *inter alia* C–H oxidative addition,[9] C–X oxidative addition,[10] and transmetallation from Ag^I precursors.[11] Most conveniently, metallation of the imidazolium C4 position can be accomplished *via* direct C–H bond activation, provided the C2 carbon is appropriately protected.[12] This method circumvents tedious pre-functionalization of the C4 position and may be applicable for a broad range of transition metals.[7,13] While crucial mechanistic details have been disclosed for the iridium- and osmium-mediated activation of the imidazolium C4–H bond,[12] little is known for the corresponding palladation reaction.

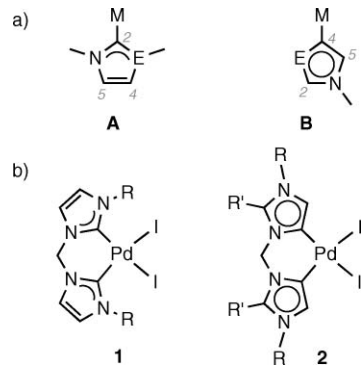

Fig. 1 a) Generic C2 and C4 bonding of imidazolium derived NHCs (**A** and **B**, respectively); b), palladium dicarbene complexes featuring normal (**1**) and abnormal bonding (**2**).

Following our preliminary communication,[14] we report here in full on the preparation and the unique reactivity of palladium(II) complexes comprising chelating C4-bound dicarbene ligands with the bonding motif **B** (**2**, Fig. 1). Since complexes **2** are active hydrogenation catalysts but their normal congeners **1** featuring the C2 bonding motif **A** are not, a special focus has been directed towards a detailed comparison of the structure and reactivity of complexes **1** and **2** (Fig. 1).

Experimental

General comments

The synthesis and spectroscopic data of the palladium complexes **2a–c**, **5**, and **6** have been reported previously.[14] All other reagents are commercially available and were used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C on Bruker spectrometers and chemical shifts (δ in ppm, coupling

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constants J in Hz) were referenced to external $SiMe_4$ (^1H, ^{13}C). Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of Ilse Beetz (Kronach, Germany).

Synthesis

General procedure for the synthesis of the diimidazolium salts 4a–d. To a solution of the 1,2-substituted imidazole **3** in toluene was added CH_2I_2 (0.5 mol equiv.). The reaction mixture was stirred at reflux temperature for 18 h. The formed precipitate was filtrated off and washed with toluene (3 × 30 mL) and Et_2O (3 × 30 mL), and dried in vacuo.

Synthesis of 4a. From 2-methyl-N-methyl imidazole **3a** (4.81 g, 50 mmol) and CH_2I_2 (6.7 g, 25 mmol) according to the general procedure. The diimidazolium salt **4a** was obtained as an off-white solid (6.97 g, 61%). An analytically pure sample was obtained by recrystallization from MeOH/Et_2O. ^1H NMR (360 MHz, DMSO-d_6): δ 7.92, 7.76 (2 × s, 2H, H_{imi}), 6.65 (s, 2H, NCH_2N), 3.78 (s, 3H, NCH_3), 2.75 (s, 3H, C_{imi}–CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 146.4 (C_{imi}–Me), 123.0 (C_{imi}), 120.9 (C_{imi}), 56.7 (NCH_2N), 35.1 (NCH_3), 10.3 (C_{imi}–CH_3). Elem. anal. calcd. for $C_{11}H_{18}I_2N_4$ (460.10): C 28.72, H 3.94, N 12.18; found: C: 29.01, H 3.97, N 11.92.

Synthesis of 4b. From 2-methyl-N-isopropyl imidazole **3b** (3.07 g, 24.07 mmol) and CH_2I_2 (3.32 g, 12.4 mmol) according to the general procedure. Compound **4b** was obtained as an off-white solid (4.35 g, 68%), which was recrystallized from MeOH at −30 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 8.00, 7.97 (2 × s, 2H, H_{imi}), 6.56 (s, 2H, NCH_2N), 4.73 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CHMe_2$), 2.82 (s, 6H, C_{imi}–CH_3), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 145.14 (C_{imi}–Me), 121.9, 118.7 (2 × C_{imi}), 56.5 (NCH_2N), 50.6 ($CHMe_2$), 21.8 ($CH(CH_3)_2$), 10.4 (C_{imi}–CH_3). Elem. anal. calcd. for $C_{15}H_{26}I_2N_4$ (516.20): C 34.90, H 5.08, N 10.85; found: C: 34.93, H 5.01, N 10.86.

Synthesis of 4c. Reaction of 2-methyl-N-mesityl imidazole **3c** (1.11 g, 5.5 mmol) and CH_2I_2 (0.74 g, 2.75 mmol) according to the general procedure gave **4c** as an off-white solid (1.32 g, 35%). An analytically pure sample was obtained by recrystallization from MeOH/Et_2O. ^1H NMR (500 MHz, DMSO-d_6): δ 8.24, 8.06 (2 × s, 2H, H_{imi}), 7.20 (s, 4H, H_{mes}), 6.80 (s, 2H, NCH_2N), 2.62 (s, 6H, C_{imi}–CH_3), 2.36 (s, 6H, C_{mes}–CH_3), 1.99 (s, 12H, C_{mes}–CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 146.8 (C_{imi}–Me), 140.9, 134.6, 129.9, 129.6 (4 × C_{mes}), 123.8, 122.4 (2 × C_{imi}), 58.2 (NCH_2N), 20.6 (C_{mes}–CH_3), 16.9 (C_{mes}–CH_3), 10.2 (C_{imi}–CH_3). Elem. anal. calcd. for $C_{27}H_{34}I_2N_4$ (668.39): C 48.52, H 5.13, N 8.38; found: C: 48.50, H 5.14, N 8.32.

Synthesis of 4d. Addition of CH_2I_2 (13.4 g, 50 mmol) to 2-phenyl-N-butyl imidazole **3d** (20.0 g, 100 mmol) according to the general procedure afforded **4d** as an off-white solid (18.70 g, 56%). Analytically pure material was obtained by recrystallization from MeOH/Et_2O. ^1H NMR (500 MHz, DMSO-d_6): δ 8.07, 7.95 (2 × s, 2H, H_{imi}), 7.72 (m, 2H, H_{aryl}), 7.60 (m, 8H, H_{aryl}), 6.30 (s, 2H, NCH_2N), 3.92 (t, $^3J_{HH}$ = 7.4 Hz, 4H, NCH_2), 1.57 (quint, $^3J_{HH}$ = 7.4 Hz, 4H, CH_2), 1.08 (sextet, $^3J_{HH}$ = 7.4 Hz, 4H, CH_2), 0.70 (t, $^3J_{HH}$ = 7.4 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 144.6 (C_{imi}–Ph), 132.9, 130.4, 129.6 (3 × C_{aryl}), 122.8, 122.2 (2 × C_{imi}), 119.6 (C_{aryl}), 57.9 (NCH_2N), 48.1 (NCH_2), 30.7 (CH_2), 18.5 (CH_2), 13.0 (CH_3). Elem. anal. calcd. for $C_{27}H_{34}I_2N_4$ (668.39) × MeOH: C 48.01, H 5.47, N 8.00; found: C: 47.88, H 5.24, N 7.98.

Synthesis of 2d. To a solution of **4d** (0.67 g, 1.0 mmol) in DMSO (5 mL) was added $Pd(OAc)_2$ (0.22 g, 1.0 mmol). The reaction mixture was stirred at 50 °C for 2 h and then at 120 °C for 3 h. After cooling to RT, CH_2Cl_2 (20 mL) and Et_2O (80 mL) were added. The formed precipitate was collected and washed repeatedly by adding CH_2Cl_2 (20 mL) followed by precipitation with Et_2O (80 mL). After drying in vacuo, complex **2d** was obtained as an off-white powder (0.42 g, 55%). An analytically pure sample was obtained by recrystallization from acetone/pentane. ^1H NMR (360 MHz, DMSO-d_6): δ 7.59 (m, 2H, H_{aryl}), 7.5–7.44 (m, 8H, H_{aryl}), 7.40 (s, 2H, H_{imi}), 5.64 (s, 2H, NCH_2N), 3.91 (t, $^3J_{HH}$ = 7.3 Hz, 4H, NCH_2), 1.55 (quint, $^3J_{HH}$ = 7.3 Hz, 4H, CH_2), 1.12 (sextet, $^3J_{HH}$ = 7.3 Hz, 4H, CH_2), 0.71 (t, $^3J_{HH}$ = 7.3, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 141.5 (C–Ph), 131.7, 130.3, 129.2 (3 × C_{aryl}), 129.2 (C_{imi}–H), 121.7 (C–Pd), 60.3 (NCH_2N), 47.0 (NCH_2), 31.5 (CH_2), 18.7 (CH_2), 13.1 (CH_3), quaternary C_{aryl} not resolved. Elem. anal. calcd. for $C_{27}H_{32}I_2N_4Pd$ (772.80): C 41.96, H 4.17, N 7.25; found: C: 41.75, H 4.51, N 7.31.

Synthesis of 7. Complex **2b** (0.40 g, 0.64 mmol) and silver acetate (0.22 g, 1.28 mmol) were stirred in MeCN (10 mL) in the dark at 60 °C for 2 d. The solution was filtered over Celite, dried over Na_2SO_4, and the solvent was removed in vacuo, thus yielding crude **7** as a waxy yellow solid (0.27 g, 87%). Colorless crystals were grown by slow diffusion of pentane into an acetone solution of **7**. ^1H NMR (360 MHz, $CDCl_3$): δ 6.35 (s, 4H H_{imi}), 6.1, 5.9 (2 × br AB doublet, 2H, NCH_2N), 4.38 (2 × sept, $^3J_{HH}$ = 6.5 Hz, 4H, $CHMe_2$), 2.77 (br s, 12H, C_{imi}–CH_3), 2.10, 1.93 (2 × s, 6H, CH_3COO), 1.3 (m, 24H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ 178.85 (MeCOO), 172.75 (MeCOO), 140.69 (C–Me), 131.87 (C–Pd), 116.65 (C_{imi}–H), 59.12 (NCH_2N), 48.95 ($CHMe_2$), 30.66 (CH_3COO), 24.29 (CH_3COO), 21.93 ($CH(CH_3)_2$), 9.53 (C_{imi}–CH_3). Elem. anal. calcd. for $C_{38}H_{60}N_8O_8Pd_2$ (969.77) × 6 H_2O: C 42.34, H 6.73, N 10.40; found: C 42.27, H 6.63, N 10.36.

Acidolysis of 2. Reactions of **2** with acids were carried out in an NMR tube in CD_3CN or DMSO-d_6 solutions using benzene as an internal standard. In a typical experiment, H_2SO_4 (40 mg, 0.41 mmol) was added to a solution of **2b** (67 mg, 0.11 mmol) and benzene (8 mg, 0.10 mmol) in CD_3CN (0.8 mL). The reaction was monitored by ^1H NMR and reached 89% conversion after 15 min and quantitative formation of **8** after 3 h. ^1H NMR (360 MHz, CD_3CN): δ 7.52 (d, 1H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.20 (d, 1H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.02 (s, 1H, H_{imi}), 6.30 (s, 2H, NCH_2N), 4.67 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, $CHMe_2$), 4.47 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, $CHMe_2$), 2.83 (s, 3H, C_{imi}–CH_3), 2.55 (s, 3H, C_{imi}–CH_3), 1.44 (d, $^3J_{HH}$ = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.39 (d, $^3J_{HH}$ = 6.6 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 145.1, 143.9 (2 × C_{imi}–Me), 121.3 (C_{imi}–H), 119.9 (C–Pd), 119.0, 118.6 (2 × C_{imi}–H), 59.0 (NCH_2N), 50.4, 50.0 (2 × $CHMe_2$), 21.9, 21.6 (2 × $CH(CH_3)_2$), 11.1, 9.8 (2 × C_{imi}–CH_3).

Synthesis of 9. A mixture of 1-isopropyl-2-methylimidazole (1.00 g, 8.0 mmol), 1-isopropylimidazole (0.91 g, 8.0 mmol) and CH_2I_2 (1.08 g, 4.0 mmol) was stirred in toluene (20 mL) at reflux

for 16 h. The formed precipitate was filtered off, washed with pentane and recrystallized from hot MeOH at-30° C to give **9** as colorless crystals (0.57 g, 27%). ^{1}H NMR (DMSO-d_6): δ 9.60, 8.06, 8.03, 7.99, 7.98 (5 × s, 1H, H_{imi}), 6.58 (s, 2H, NCH_2N), 4.71 (2 × sept, $^3J_{HH}$ = 6.4 Hz, 2H, $CHMe_2$), 2.83 (s, 3H, C_{imi}–CH_3), 1.50, 1.43 (2 × d, $^3J_{HH}$ = 6.4 Hz, 6H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 146.21, 137.03, 123.25, 122.47, 122.12, 119.60 (6 × C_{imi}), 57.90 (NCH_2N), 53.64 ($CHMe_2$), 51.39 ($CHMe_2$), 22.93 ($CH(CH_3)_2$), 22.60 ($CH(CH_3)_2$), 11.29 (C_{imi}–CH_3). Elem. anal. calcd. for $C_{14}H_{24}N_4I_2$ (502.18): C, 33.48; H, 4.82; N, 11.16. Found: C, 33.57; H, 4.72; N, 11.02.

Synthesis of 11. To a solution of the diimidazolium salt **9** (0.50 g, 1.0 mmol) in DMSO (10 mL) was added [$Pd(OAc)_2$] (0.22 g, 1.0 mmol) and the mixture was stirred at 50° C for 2 h and at 110 °C for another 3 h. After cooling, CH_2Cl_2 (20 mL) was added followed by Et_2O (100 mL). The formed precipitate was collected by centrifugation and washed by repetitive addition of CH_2Cl_2 and subsequent precipitation with Et_2O to afford **11** as a yellow powder (0.42 g, 63%). An analytically pure sample was obtained by recrystallization from MeCN/Et_2O. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.93 (s, 2H, H_{imi}), 7.80, 7.73 (2 × s, 1H, H_{imi}), 6.46 (s, 2H, NCH_2N), 5.30 (br, 1H, $CHMe_2$), 4.74 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, $CHMe_2$), 3.1 (br s, 3H, C_{imi}–CH_3), 1.44, 1.40 (2 × d, $^3J_{HH}$ = 6.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 144.34 (C_{imi}–Me), 125.30, 121.33, 119.28, 118.77 (4 × C_{imi}), 118.02 (C–Pd), 59.65 (NCH_2N), 53.24 (br, $CHMe_2$), 50.29 ($CHMe_2$), 21.98 ($CH(CH_3)_2$), 21.06 ($CH(CH_3)_2$), 12.30 (br, C_{imi}–CH_3). Elem. anal. calcd. for $C_{14}H_{23}I_3N_4Pd$ (734.49) × 0.5 MeCN: C, 23.86; H, 3.27; N, 8.35. Found: C, 24.35; H, 3.56; N, 8.17.

Crystal structure determinations†

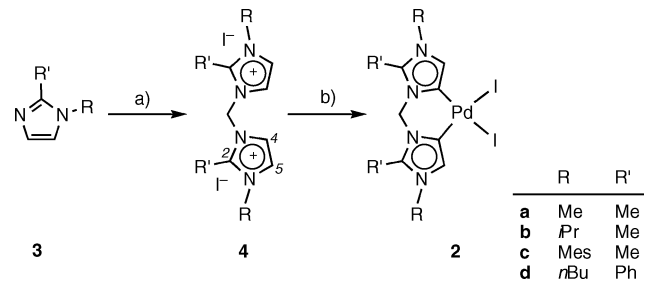
Suitable single crystals were mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite-monochromator. Data collection was performed at −100 °C using Mo-Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 70 mm (for **2d**, **7**, and **11**) and 135 mm (for **2a** and **2c**), respectively. All structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least squares on F^2 with SHELXL-97.[15] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically, except for partically occupied solvent atoms, which were refined isotropically. A semi-empirical absorption correction was applied using MULscanABS as implemented in PLATON03.[16]

The complex molecule in crystals of **2a** adopts two different orientations. As a consequence, all atom positions are half occupied. In addition, one disordered acetonitrile molecule co-crystallized with an occupancy factor for all atoms of 0.25. Complex **2d** crystallized with two complex molecules in the asymmetric unit. Two butyl groups of the ligand in one of the complex molecules are disordered. The involved carbon atoms were refined with occupancies of 0.5 and their thermal values were constrained to be equal. The co-crystallized pentane molecule is strongly disordered. The SQUEEZE option in PLATON03 was used to allocate the electron density corresponding to the pentane molecule (201 Å^3 containing and about 32 electrons; one pentane molecule requires 42 electrons), which was included in all further calculations. The binuclear complex **7** crystallized with two acetate anions (three positions, two of them are half occupied), one pentane (half occupied) and one water molecule (occupancy 0.25, hydrogen atoms not localized) in the asymmetric unit. The two half-occupied acetate anions are disordered, and therefore their bond distances and thermal values were constrained. Crystals of complex **11** contain two palladium complexes and one molecule of MeCN in the asymmetric unit. In each of the two independent complex molecules, one isopropyl group was found to be disordered over two positions (occupancies 0.5). Further details on data collection and refinement parameters are collected in Table 1.

Results and discussion

Synthesis of complexes

The 2,2′-disubstituted imidazolium salts **4a–d** were prepared by quaternization of the corresponding N-functionalized 2-methyl or 2-phenyl imdazoles **3a–d** with CH_2I_2. Subsequent palladation with $Pd(OAc)_2$ according to established procedures[14,17] induced C–H bond activation and afforded the palladium complexes **2a–d** containing C4-bound dicarbene ligands[18] as off-white air-stable solids (Scheme 1). Yields are generally excellent (>90%), indicating that competing side reactions are negligible. In particular, no C–H bond activation of the methyl group in C2 position has been observed with ligands **4a–c**, thus contrasting the reactivity of similar imidazolium salts towards silver(I) and iridium(III) precursors.[19] Since the reaction conditions used for preparing the dicarbene complexes **1** and **2** are very similar, it seems that the pK_a values of the C2-bound proton in the precursor of **1** and of C4–H in **4** may be less separated than the theoretically predicted 8 pK_a units (calculated pK_a 24 and 32, respectively).[20] Clearly however, functionalization of the imidazolium C2 position is mandatory for directing the regioselectivity of C–H bond activation to the C4 position.[17,21]



	R	R′
a	Me	Me
b	*i*Pr	Me
c	Mes	Me
d	*n*Bu	Ph

Scheme 1 *Reagents and conditions:* a) CH_2I_2, toluene, reflux; b) $Pd(OAc)_2$, DMSO, 50 °C to 120 °C.

Successful cyclopalladation is indicated by the pertinent NMR spectroscopic data of the complexes **2**. Notably, the methylene group interlinking the two metallated heterocycles appears as a singlet in the ^{1}H NMR spectrum (δ_H 6.1). The magnetic equivalence of the two CH_2 protons indicates a flexible conformation of the metallacycle. In the ^{13}C NMR spectrum, the metal-bound carbon appears around δ_C 120–124, which is virtually at the same frequency as in the imidazolium precursors. This comparable substituent effect of a hydrogen and a palladium(II) center on the C4 chemical shift points to a relatively low carbene contribution to the Pd–C bond in complexes **2**. In the corresponding

Table 1 Crystallographic data for complexes **2a**, **2c**, **2d**, **7**, and **11**

	2a	**2c**	**2d**	**7**	**11**
Color, shape	Orange rod	Light brown block	Orange rod	Yellow block	Orange needle
Size/mm	0.25 × 0.10 × 0.10	0.25 × 0.20 × 0.15	0.35 × 0.30 × 0.25	0.45 × 0.40 × 0.35	0.45 × 0.25 × 0.15
Empirical formula	$C_{11}H_{16}I_2N_4Pd\cdot 0.5CH_3CN$	$C_{27}H_{32}I_2N_4Pd$	$C_{27}H_{32}I_2N_4Pd\cdot 0.25C_5H_{12}$	$C_{38}H_{60}N_8O_8Pd_2\cdot 0.5C_5H_{12}\cdot 0.25H_2O$	$C_{14}H_{23}I_3N_4I_3Pd\cdot 0.5CH_3CN$
Fw	585.01	772.77	790.80	1010.32	754.99
T/K	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	*Pbam* (No. 55)	P_{-1} (No. 2)	P_{-1} (No. 2)	P_{-1} (No. 2)	$P2_1/a$ (No. 14)
Unit cell					
a/Å	13.7424(13)	9.8664(11)	12.8204(15)	13.1967(10)	13.9765(12)
b/Å	18.4993(17)	12.3939(15)	15.0692(17)	13.7943(11)	9.9155(6)
c/Å	6.9570(7)	12.8016(13)	16.8311(19)	16.4100(12)	33.885(3)
α/deg	90	66.710(8)	94.572(13)	68.202(8)	90
β/deg	90	83.725(9)	107.296(13)	69.115(9)	97.039(10)
γ/deg	90	78.530(9)	104.040(13)	86.363(9)	90
V/Å^3	1768.6(3)	1408.3(3)	2971.1(6)	2583.2(4)	4660.6(6)
Z	4	2	4	2	8
D_{calc}/g cm^{-3}	2.197	1.822	1.768	1.299	2.152
μ/mm^{-1} (Mo K$_\alpha$)	4.536	2.873	2.726	0.747	4.776
No. of total, unique reflns	20143, 1725	15991, 5004	23096, 10901	20450, 9375	31627, 9055
R_{int}	0.0539	0.0385	0.0633	0.0425	0.0450
Transmission range	0.458–0.582	0.619–0.678	0.437–0.476	0.776–0.825	0.252–0.296
No. paras, restr.	157, 2	315, 0	552, 12	529, 15	408, 8
R_1[a] wR_2[b] for $I > 2\sigma(I)$	0.0421, 0.1153	0.0262, 0.0570	0.0499, 0.1135	0.0496, 0.1470	0.0327, 0.0819
R_1[a] wR_2[b] for all I	0.0481, 0.1178	0.0401, 0.0598	0.1108, 0.1261	0.0738, 0.1574	0.0530, 0.0989
GOF	1.247	0.936	0.748	0.984	0.909
Min/max resid density/e Å^{-3}	–0.713, 1.693	–0.592, 0.777	–1.423, 1.280	–0.826, 1.107	–1.861, 1.623

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(w(F_o^4)]^{1/2}$.

C2-bound dicarbene complexes **1** (δ_C around 160), palladation induces typically a lowfield shift of around 20 ppm for the metal-bound carbon.

Solid state structures

Further structural information was obtained by crystallographic analysis of the C4-bound dicarbene palladium complexes. The molecular structures of the complexes **2a**, **2c**, and **2d** are depicted in Fig. 2 and reveal several common features. The palladium center is generally located in a distorted square-planar environment with (pseudo-)C_{2v} symmetry. The bite angle of the chelating dicarbene is slightly smaller than 90° and hence well-suited for stabilizing square-planar or octahedral coordination geometries.

Table 2 lists the pertinent bond distances and angles of the new structures of **2a**, **2c**, and **2d**. It is particularly instructive to compare these geometrical data with those available for the known[22] C2-bound dicarbene analogues **1**. For example, the Pd–C bond length is identical within standard deviations in all complexes, averaging to 1.98(2) Å in C4-bound dicarbenes and 1.99(1) Å in C2-bound systems. Apparently, the Pd–C bond length is encoded by the size of, and the hybridization within the metallacycle. Similarly the Pd–I bond distances are statistically equal, averaging to 2.673(15) Å in complexes **2** and to 2.658(11) Å in the C2-bound complexes **1**.

This Pd–I bond length analysis may hence point to a virtually identical *trans* influence of the two NHC isomers, although steric factors need to be considered as well. Repulsion of the halide from the metal coordination sphere due to the presence of substituents R at nitrogen (Scheme 1) is expected to be more pronounced in the C2-bound carbene[22f] than in the C4-bound ligand. Possibly, these steric effects compensate a potentially stronger *trans* influence of the C4-bound carbene. Such a hypothesis is further supported by the different torsion of the heterocycles with respect to the palladium square plane. In the C2-bound carbene complexes **1**, the heterocycles are twisted 45–62° out of the coordination plane.[22] In the C4-bound carbene complexes, which comprise only a hydrogen rather than an alkyl group at the α-positioned atom, these dihedral angles are significantly smaller (N–C–Pd–C between 28° and 41°). A further difference concerns the heterocyclic C–C bond. In the C4-bound carbene complexes **2**, the average of this bond is 1.368(18) Å and represents a conjugated double bond, while in the C2-bound ligands, the short 1.336(11) distance rather indicates a localized olefinic bond. A similar trend has been observed in related iridium and rhodium chemistry[7a,11] and suggests a different

Table 2 Selected bond lengths (Å) and angles (deg) of complexes **2a**, **2c**, and **2d**

			2d	
	2a	**2c**	Molecule 1	Molecule 2
Pd1–C1	1.994(17)	1.990(4)	1.966(10)	1.966(10)
Pd1–C7	2.014(17)	1.994(4)	1.990(9)	1.995(9)
Pd1–I1	2.6558(12)	2.6522(5)	2.6747(10)	2.6832(11)
Pd1–I2	2.6835(12)	2.6998(5)	2.6619(11)	2.6569(10)
N2–C1	1.40(2)	1.401(5)	1.403(12)	1.393(11)
N3–C7	1.39(2)	1.411(5)	1.407(12)	1.398(12)
C1–C2	1.37(3)	1.358(5)	1.376(13)	1.368(12)
C6–C7	1.35(2)	1.358(5)	1.366(12)	1.337(13)
C1–Pd1–C7	87.3(8)	86.68(15)	87.1(4)	86.4(4)
I1–Pd1–I2	91.81(4)	92.59(15)	93.83(4)	93.75(3)
N2–C1–Pd–C7	29.7(16)	28.3(3)	30.0(7)	37.2(7)
N3–C7–Pd–C1	30.3(15)	29.4(3)	28.4(7)	32.7(8)

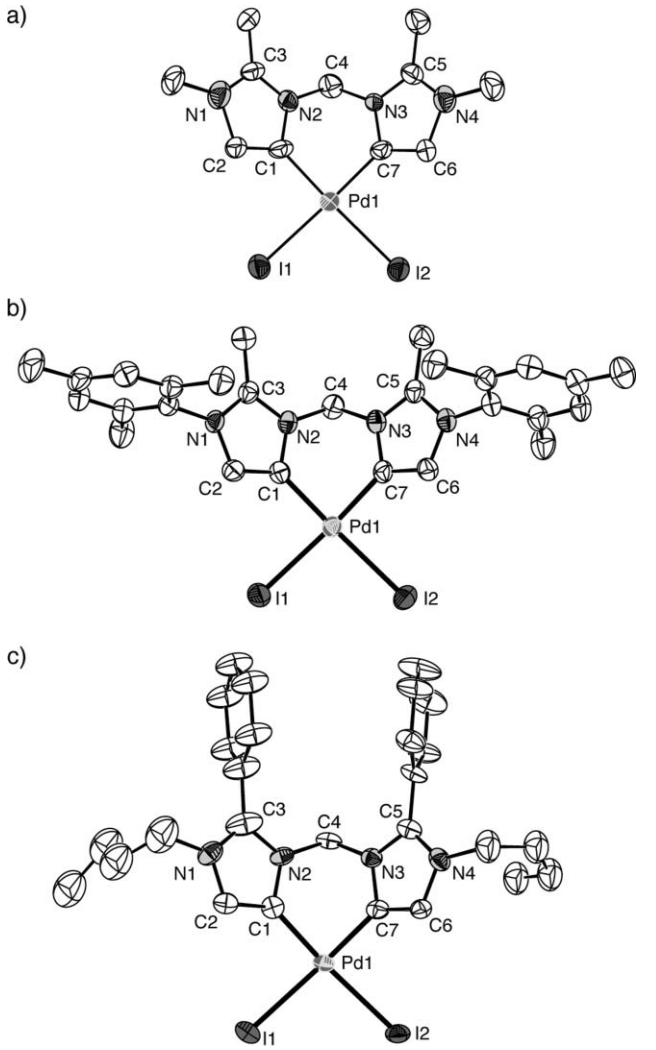
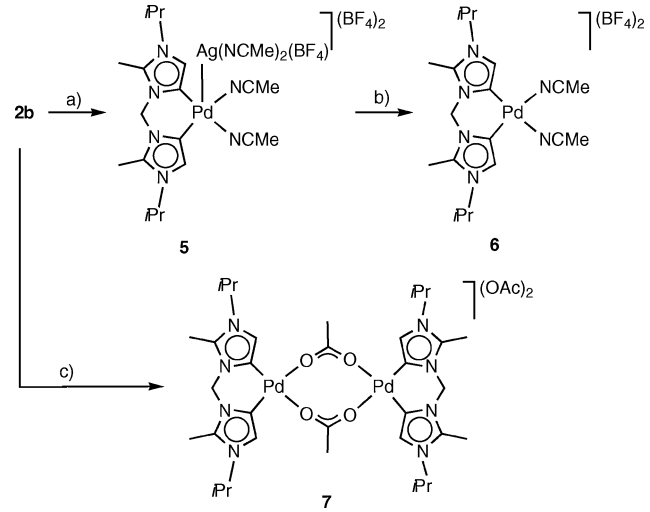


Fig. 2 ORTEP representation of complexes **2a** (a; 50% probability), **2c** (b; 50% probability), and **2d** (c; 30% probability). All hydrogen atoms, co-crystallized solvent molecules, and the second molecule in the asymmetric unit of **2d** have been omitted for clarity. Only one of the two disordered orientations of **2a** is shown.

bonding situation within the isomeric heterocycles in complexes **1** and **2**. This conclusion corroborates the NMR analyses in solution (see above).

Impact of C4 bonding on reactivity

In the presence of silver(I) ions, the C4-bound carbene complexes **2** exhibit unique reactivity patterns. Most metal-halide complexes, including the C2-bound dicarbene complexes **1**, undergo ligand exchange and yield the corresponding cationic solvento complexes. In contrast, exposure of complex **2** in MeCN to $AgBF_4$ does not only induce the expected halide abstraction from the metal coordination sphere, but simultaneously, the adduct **5** is formed (Scheme 2). Crystallographic analysis unequivocally revealed the formation of the five-coordinate palladium complex **5** comprising unusually[23] short Ag · · · Pd contacts of 2.8701(6) Å. The molecular structure of this adduct has been preliminarily reported.[14] Bonding analysis identifies the palladium center as a Lewis basic site, despite its formally dicationic charge. The behavior of palladium



Scheme 2 *Reagents and conditions:* a) $AgBF_4$, MeCN; b) DMSO or MeOH; c) AgOAc, DMSO.

as ligand[24] to silver presumably originates from the strong donor ability of the C4-bound dicarbene ligand.

Silver decoordination and formation of the bissolvento complex **6** has been achieved by dissolving complex **5** in DMSO or MeOH. These solvents appear to be nucleophilic enough to successfully compete with the palladium center for silver coordination, while MeCN is not. Accordingly, the direct synthesis of the bissolvento complex **6** from the neutral complex **2** is best performed by using 3 mol equiv. $AgBF_4$ followed by a work-up that includes a $MeOH/Et_2O$ precipitation sequence.

The different reactivity of the palladium complexes **1** and **2** towards Ag^+ coordination provides a qualitative probe for the donor ability of the palladium center relative to various solvents, increasing in the order Pd(C2-dicarbene) < MeCN < Pd(C4-dicarbene) < MeOH, DMSO. From this sequence, it is obvious that the C4-bonding mode increases the electron density at the metal center as compared to C2-bound carbene ligands.

When using different silver(I) precursors, charge compensation at the palladium may occur along other pathways. For example with 2 mol equiv. Ag(OAc), formation of the dimeric species **7** was observed. Crystallographic analysis of complex **7** shows an open book type structure (Fig. 3). The Pd · · · Pd distance is 2.9441(6) Å and hence comparable to related acetate-bridged palladium(II) dimers,[25] though significantly shorter than the sum of the van der Waals radii (3.30 Å).[26] Notably under identical reaction conditions, the analogous C2-bound dicarbene complexes provide monomeric complexes containing two κ^1-bound acetates.[27] Anion exchange was recently reported to yield a dimeric structure that is closely related to that of **7**.[28] However, the Pd · · · Pd distance in the C2-bound analogue (3.1683(6) Å) is substantially larger than that of **7**.

Complex **7** is only sparingly soluble in most organic solvents. Its ^{1}H NMR spectrum in DMSO-d_6 solution shows unusually broad features which do not sharpen upon heating up to 100 °C. This may point to a geometrically constrained structure in solution and hence to a conservation of the rigid geometry as determined by solid state analysis. This is further supported by the observation of two acetate signals in 1:1 molar ratio at δ_C 1.93 and 2.10. The low shift of the latter resonance is indicative for cationic palladium

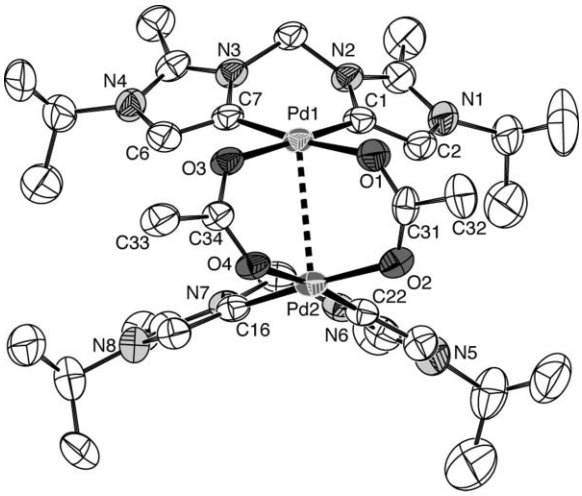
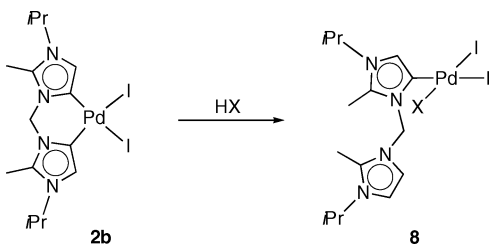


Fig. 3 Thermal ellipsoid plot (50% probability) of the dimeric complex **7**. Selected bond lengths (Å): Pd1–C1 1.951(5), Pd1–C7 1.947(6), Pd1–O1 2.098(4), Pd1–O3 2.087(4), Pd2–C16 1.955(5), Pd1–C7 1.932(6), Pd2–O2 2.089(4), Pd2–O4 2.098(3), Pd1 ··· Pd2 2.9441(6); selected bond angles (deg): C1–Pd1–C7 87.4(2), O1–Pd1–O3 90.68(17), C16–Pd2–C22 87.4(2), O2–Pd2–O4 90.68(16).

acetate complexes.[28,29] The ^{13}C NMR signals are better resolved and display a resonance for the metal-bound carbon at δ_C 132. This frequency corresponds to a downfield shift as compared to the neutral diiodide precursor **2b** and may be attributed in parts to the different donor power of OAc^- and I^-.

The ability of complexes **2a–d** to bind Ag^+ ions reflects the Lewis basic character of the palladium center. Likewise, these complexes also display Brønsted basic properties. Addition of H_2SO_4 (5 mol equiv.) to complex **2** induced rapid palladium–carbene bond cleavage. Spectroscopic analysis of the product indicates the cleavage of one Pd–C bond only and formation of the monocarbene complex **8** (eqn (1), X presumably HSO_4). Three different proton signals are visible in the 7–7.5 ppm range, two of which are mutually coupled ($^3J_{HH}$ = 2.2. Hz) and were therefore assigned to the imidazolium residue of **8**. Likewise, two sets of methyl and isopropyl groups appeared in a 1:1 ratio.



2b **8** (1)

In MeCN or DMSO, acidolysis is fast at RT (<15 min). No further reaction was observed, even when keeping complex **8** in the presence of excess H_2SO_4 at 80 °C for several hours. Lowering the H_2SO_4 concentrations led to partial acidolysis only, *e.g.* 2.2 mol equiv. H_2SO_4 gave an approximate 2:1 mixture of **8** and **2**. With weaker acids such as H_3PO_4, heating to 85 °C is required in order to initiate Pd–C bond cleavage. No reaction occurs with very weak acids (HOAc), even at elevated temperature. The stability of the $Pd–C_{carbene}$ bonds in complexes **2** and **8** towards HOAc suggests that the opposite process of the acidolysis, that is the metallation of the diimidazolium salt with $Pd(OAc)_2$, is irreversible and hence kinetically controlled.

Acidolysis of the Pd–C bond in complex **2** may involve formation of an intermediate palladium-hydrogen adduct in analogy to the reaction of **2** with $AgBF_4$ (*cf.* adduct **5**, Scheme 2). A subsequent hydrogen shift from palladium to carbon would induce Pd–C bond cleavage. Attempts to detect the surmised metal-bound hydrogen by in situ NMR spectroscopy have failed thus far. Participation of the metal center in the acidolysis reaction as opposed to direct attack at the metal-bound carbon is supported, however, by the fact that only one metal–carbene bond of **2** is broken, while the monocarbene complex **8** is acid-stable. Obviously, forthcoming studies need to address also other factors, such as the electrostatic protection of the metal center in **8** by the dangeling cationic imidazolium residue.

Notably, the bissolvento complex **6** undergoes similar acid-mediated Pd–C bond cleavage and forms a monocarbene complex related to **8**, while the C2-bound dicarbene complexes **1** are completely stable towards strong acids (H_2SO_4), even upon heating to 80 °C for prolonged time. This different stability properties indicate that the carbene bonding mode influences the reactivity of the coordinated metal center considerably more than the ancillary ligands do, in particular when using polar solvents. The reactivity of complex **2** but not **1** with acids lends further[7,11,14] support to the notion that C4-bound carbenes are ligands with exceptionally strong donor ability.

Mechanistic aspects of C4 metallation

The stability of complexes **2** and **8** towards HOAc (see above) implies that the palladium-carbene bond formation is an irreversible processes.[30] This resistence towards Pd–C bond cleavage excludes chelation as a driving force for the *first* metallation, *i.e.* the formation of a product similar to **8**. In this light, the regioselectivity of the palladation is remarkable, also because of the similar acidity of the C4–H and C5–H protons in the imidazolium ligand precursor salt **4**. Hence a pre-equilibrium must exist, in which the metal center is directed towards the C4–H bond. Steric arguments would fall short, given the high yield of cyclopalladated product is independent of the wingtip group R (*e.g.* R = Me, Mes). Herrmann and coworkers observed the presence of the dianionic palladate $[PdI_2(OAc)_2]^{2-}$ prior to palladation of related diimidazolium salts at the C2 position.[22b] Similar palladate formation and concomitant ion pairing with the diimidazolium dication (**C**, Fig. 4) may provide a rationale for the selective activation of the (inner) C4–H rather than the more remote C5–H bond from **C**.[31] The relevance of a putative ion pair complex is further strengthened by the fact that all our palladation attempts using diimidazolium salts containing BF_4^- counteranions were unsuccessful. C–H bond activation from the ion pair **C**, perhaps mediated by a bridging coordination mode of the acetate ligands, affords the monocarbene intermediate **E**, or **D** if the C2 position is not substituted (Fig. 4). An analog of **D** has been isolated and structurally characterized (R = *t*Bu).[22b] Cyclometallation from **D** or **E** may then occur along established pathways.[32]

A potential driving force for the cyclometallation step has been deduced from palladation experiments using the dissymmetric diimidazolium salt **9** (Scheme 3).[33] Metallation of **9** under the

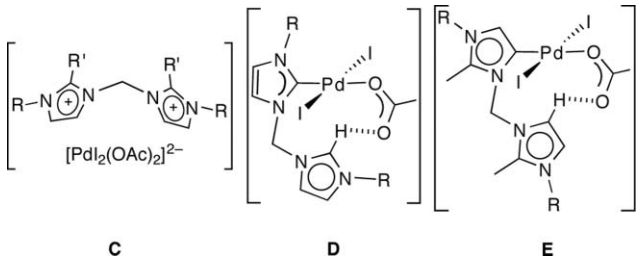
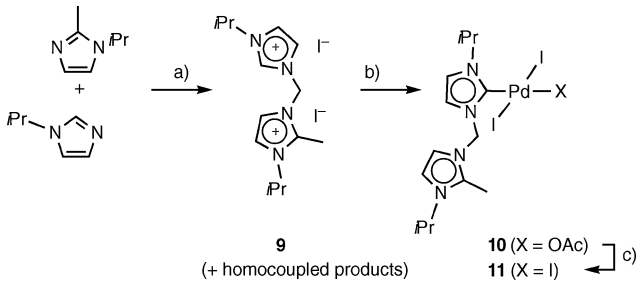


Fig. 4 Proposed intermediates for the palladation of imidazolium cations *via* C4–H bond activation: ion pair complex **C** preceding the first C–Pd bond formation with high regioselectivity for C4–H bond activation; macrocyclic complexes **D** and **E** for inducing cyclometallation at the C2 and the C4 position, respectively.



Scheme 3 *Reagents and conditions:* a) CH_2I_2, toluene, reflux, then recrystallization; b) $Pd(OAc)_2$, DMSO, 50 °C to 120 °C; c) NaI, acetone.

conditions applied previously for the palladation of **4** gave the monocarbene complex **10** as the major product. Upon work-up, anion metathesis took place, leading to the formation of complex **11** comprising three iodide ligands at palladium. Complex **11** was unambiguously characterized by single crystal X-ray diffraction (Fig. 5). In the ^{1}H NMR spectrum, the presence of three different aromatic signals at δ_H 7.93, 7.80, and 7.73 (2:1:1 ratio) was diagnostic. No cyclometallation could be induced by heating either complex **10** or the in situ formed complex **11** for prolonged periods of time, and instead only slow decomposition was observed. Apparently, C4–H bond activation is considerably more difficult in complex **10** and **11** than in the related intermediate **E**.

The bonding mode of the carbene is the most notable difference between the stable complex **10** and the proposed intermediate **E**. Hence, cyclometallation *via* C–H bond activation from monocarbene complexes seems to be crucially depending on i) the electron density at palladium and ii) the acidity of the C–H proton. Thus, activation of a less acidic C4–H bond[20] requires an increased basicity of the acetate ligand, which is apparently generated in a C4-bound (*cf.* **E**) but not in a C2-bound monocarbene intermediate such as **10**. In contrast C2–H bond activation occurs also with less basic acetates as in the monocarbene intermediate **D**. Such a model is in line with the concept of C4-bound carbenes as substantially stronger donors than C2-bound carbenes. In addition, it may rationalize the similar conditions required for the preparation of the cyclopalladated complexes **2** and **1**. Clearly, further studies are warranted to verify and refine this model.

Conclusions

Palladium complexes comprising C4-bound imidazolium-derived dicarbene ligands have been prepared and their reactivity properties have been characterized. All evidence suggests that the palladium center is a stronger Lewis (and probably also Brønsted) base when coordinated by C4-bound dicarbene ligands as opposed to C2-bound analogues. This may be attributed to a more pronounced zwitterionic bonding of C4-carbenes, comprising a anionic vinyl-type fragment for metal coordination and a cationic NCN amidinium residue for intramolecular charge compensation. Irrespective of the exact bond description, the substantially higher donor power of C4-bound carbenes is expected to have a strong impact on the catalytic activity of the coordinated metal center and may disclose new applications beyond H_2 activation and hydrogenation. Studies along these lines are currently in progress in our laboratories.

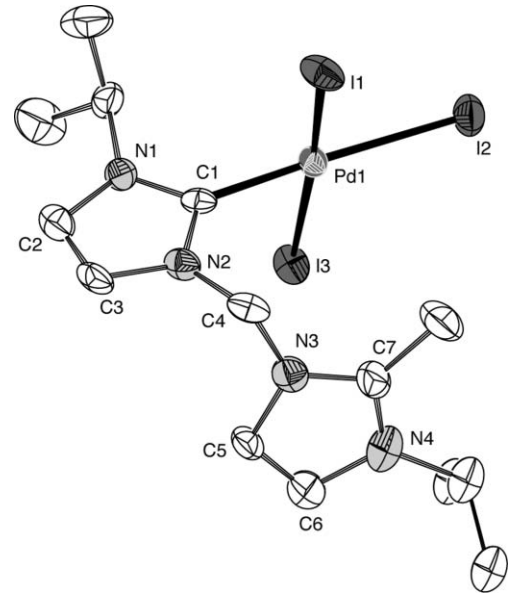


Fig. 5 Thermal ellipsoid plot (50% probability) of the monocarbene complex **11** (50% probability, only one of the two crystallographically independent molecules shown). Selected bond lengths (Å): Pd1–C1 1.968(6), Pd1–I1 2.6302(7), Pd1–I2 2.6751(7), Pd1–I3 2.6162(7), C2–C3 1.328(10), C5–C6 1.340(10); selected bond angles (deg): C1–Pd1–I1 87.89(18), C1–Pd1–I2 177.37(17), C1–Pd1–I3 85.59(18), I1–Pd1–I3 172.33(2).

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Notes and references

1 (*a*) D. Bourissou, O. Guerret, F. Gabbai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39; (*b*) V. Cesar, S. Bellemin-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619; (*c*) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122 For most recent highlights in this area, see; (*d*) O. Kaufhold and F. E. Hahn, *Angew. Chem. Int. Ed.*, 2008, **47**, 4057.

2 (*a*) W. A. Herrmann, *Angew. Chem. Int. Ed.*, 2002, **41**, 1290; (*b*) *N-heterocyclic carbenes in synthesis*, ed. S. P. NolanWiley-VCH, Weinheim, 2006; (*c*) A. T. Normand and K. J. Cavell, *Eur. J. Inorg. Chem.*, 2008, 2781.

3 (*a*) T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson, R. J. Holmes and S. R. Forrest, *Inorg. Chem.*, 2005,

44, 7992; (*b*) D. M. Khramov, A. J. Boydston and C. W. Bielawski, *Angew. Chem. Int. Ed.*, 2006, **45**, 6186; (*c*) L. Mercs, A. Neels and M. Albrecht, *Dalton Trans.*, 2008, DOI: 10.1039/b809721f.

4 (*a*) A. A. Danopoulos, N. Tsoureas, J. C. Green and M. B. Hursthouse, *Chem. Commun.*, 2003, 756 Notably, the metal-carbene bond in NHC complexes may participate in reactions and may not be innocent. For examples, see; (*b*) K. J. Cavell and D. S. McGuinness, *Coord. Chem. Rev.*, 2004, **248**, 671; (*c*) S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey and J. M. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 13702; (*d*) B. K. Shaw, T. Steinke and M. D. Fryzuk, *XXIII International Conference on Organometallic Chemistry*, abstract P756.

5 (*a*) R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen and M. J. Quayle, *Chem. Commun.*, 1999, 241; (*b*) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 2274; (*c*) C. C. Scarborough, M. J. W. Grady, I. A. Guzei, B. A. Gandhi, E. E. Bunel and S. S. Stahl, *Angew. Chem. Int. Ed.*, 2005, **44**, 5269; (*d*) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.*, 2005, **44**, 5705; (*e*) V. Lavallo, Y. Canac, A. DeHope, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.*, 2005, **44**, 7236; (*f*) S. Gomez-Bujedo, M. Alcarazo, C. Pichon, E. Alvarez, R. Fernandez and J. M. Lassaletta, *Chem. Commun.*, 2007, 1180; (*g*) Y. Han, H. V. Huynh and G. K. Tan, *Organometallics*, 2007, **26**, 6581; (*h*) H. G. Raubenheimer and S. J. Cronje, *Dalton Trans.*, 2008, 1265; (*i*) M. A. Esteruelas, F. J. Fernandez-Alvarez and E. Onate, *J. Am. Chem. Soc.*, 2006, **128**, 13044; (*j*) E. Alvarez, S. Conejero, M. Paneque, A. Petronilho, M. L. Poveda, O. Serrano and E. Carmona, *J. Am. Chem. Soc.*, 2006, **128**, 13060; (*k*) C. E. Ellul, M. F. Mahon, O. Saker and M. K. Whittlesey, *Angew. Chem. Int. Ed.*, 2007, **46**, 6343; (*l*) M. Iglesias, D. J. Beetstra, A. Stasch, P. N. Horton, M. B. Hursthouse, S. J. Coles, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2007, **26**, 4800For different engineering of the basicity of carbenes, see:; (*m*) D. M. Khramov, V. M. Lynch and C. W. Bielwaski, *Organometallics*, 2007, **26**, 6042; (*n*) A. Fürstner, M. Alcarazo, H. Krause and C. W. Lehmann, *J. Am. Chem. Soc.*, 2007, **129**, 12676.

6 S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 2274.

7 (*a*) L. Yang, A. Krüger, A. Neels and M. Albrecht, *Organometallics*, 2008, **27**, 3161; (*b*) M. Albrecht, *Chem. Commun.*, 2008, 3601.

8 P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596.

9 D. Bacciu, K. J. Cavell, I. A. Fallis and L.-I. Ooi, *Angew. Chem. Int. Ed.*, 2005, **44**, 5282.

10 E. Kluser, A. Neels and M. Albrecht, *Chem. Commun.*, 2006, 4495.

11 (*a*) A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller and R. H. Crabtree, *Organometallics*, 2004, **23**, 2461; (*b*) G. Song, Y. Zhang and X. Li, *Organometallics*, 2008, **27**, 1936.

12 (*a*) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *J. Am. Chem. Soc.*, 2002, **124**, 10473 In some cases, C2 protection is not necessary, see; (*b*) L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 2005, **127**, 16299; (*c*) M. Baya, B. Eguillor, M. A. Esteruelas, M. Loivan and E. Onate, *Organometallics*, 2007, **26**, 6556; (*d*) B. Eguillor, M. A. Esteruelas, M. Olivan and M. Puerta, *Organometallics*, 2008, **27**, 445.

13 (*a*) G. Song, X. Wang, Y. Li and X. Li, *Organometallics*, 2008, **27**, 1187; (*b*) H. Lebel, M. K. Janes, A. B. Charette and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5046; (*c*) L. Campeau, P. Thansandote and K. Fagnou, *Org. Lett.*, 2005, **7**, 1857; (*d*) M. Alcarazo, S. J. Roseblade, A. R. Cowley, R. Fernandez, J. M. Brown and J. M. Lassaletta, *J. Am. Chem. Soc.*, 2005, **127**, 3290.

14 M. Heckenroth, E. Kluser, A. Neels and M. Albrecht, *Angew. Chem. Int. Ed.*, 2007, **46**, 6293.

15 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.

16 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

17 (*a*) M. G. Gardiner, W. A. Herrmann, C.-P. Reisinger, J. Schwarz and M. Spiegler, *J. Organomet. Chem.*, 1999, **572**, 239; (*b*) M. V. Baker, B. W. Skelton, A. H. White and C. C. Williams, *J. Chem. Soc. Dalton Trans.*, 2001, 111; (*c*) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller and R. H. Crabtree, *Organometallics*, 2002, **21**, 700.

18 The metal-bound carbons in complex **2a** should formally be labeled as C5 carbons. For reasons of consistency, however, we use here only the atom labeling scheme depicted in Scheme 1.

19 (*a*) A. R. Chianese, B. M. Zeglis and R. H. Crabtree, *Chem. Commun.*, 2004, 2176; (*b*) M. Viciano, M. Feliz, R. Corberan, J. A. Mata, E. Clot and E. Peris, *Organometallics*, 2007, **26**, 5304.

20 (*a*) A. M. Magill and B. F. Yates, *Aust. J. Chem.*, 2004, **57**, 1205; (*b*) R. W. Alder, P. R. Allen and S. J. Williams, *J. Chem. Soc. Chem. Commun.*, 1995, 1267 For experimentally determined pK_a of the C2–H proton, see; (*c*) T. L. Amyes, S. T. Diver, J. P. Richard, F. M. Rivas and K. Toth, *J. Am. Chem. Soc.*, 2004, **126**, 4366; (*d*) A. M. Magill, K. J. Cavell and B. F. Yates, *J. Am. Chem. Soc.*, 2004, **126**, 8717.

21 (*a*) D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.*, 2001, **123**, 8317 The same conclusion has been drawn for palladation *via* C–H bond oxidative addition: see ref. 9 and; (*b*) S. Gründemann, M. Albrecht, A. Kovacevic, J. W. Faller and R. H. Crabtree, *J. Chem. Soc., Dalton Trans.*, 2002, 2163.

22 (*a*) W. A. Herrmann, C.-P. Reisinger and M. Spiegler, *J. Organomet. Chem.*, 1998, **557**, 93; (*b*) W. A. Herrmann, J. Schwarz and M. G. Gardiner, *Organometallics*, 1999, **18**, 4082; (*c*) F. E. Hahn and M. Foth, *J. Organomet. Chem.*, 1999, **585**, 241; (*d*) J. Schwarz, V. P. W. Böhm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer and G. Raudaschl-Sieber, *Chem. Eur. J.*, 2000, **6**, 1773; (*e*) S. Ahrens, A. Zeller, M. Taige and T. Strassner, *Organometallics*, 2006, **25**, 5409; (*f*) M. Heckenroth, A. Neels, H. Stoeckli-Evans and M. Albrecht, *Inorg. Chim. Acta*, 2006, **359**, 1929; (*g*) M. Nonnenmacher, D. Kunz, F. Rominger and T. Oeser, *J. Organomet. Chem.*, 2007, **692**, 2554.

23 (*a*) Y. Liu, K. H. Lee, J. J. Vittal and T. S. A. Hor, *J. Chem. Soc., Dalton Trans.*, 2002, 2747; (*b*) J. Forniés and A. Martin, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, Weinheim, 1999, vol. 1, p. 417.

24 For a review on the complex-as-ligand concept, see E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y. Journaux, F. Lloret and M. Julve, *Dalton Trans.*, 2008, 2780.

25 A CCDC search on acetate-bridged palladium dimers returned 130 hits with an average Pd···Pd distance of 2.991(11) Å. About 50% of the found complexes display a Pd···Pd distance in the 2.82–2.96 Å range.

26 T. W. Hambley, *Inorg. Chem.*, 1998, **37**, 3767.

27 W. A. Herrmann, J. Schwarz, M. G. Gardiner and M. Spiegler, *J. Organomet. Chem.*, 1999, **575**, 80.

28 J. C. Slootweg and P. Chen, *Organometallics*, 2006, **25**, 5863.

29 N. Thirupathi, D. Amoroso, A. Bell and J. D. Protasiewicz, *Organometallics*, 2005, **24**, 4099.

30 Similar conclusions have been drawn from different experiments, see ref. 22*f* and C. Köcher and W. A. Herrmann, *J. Organomet. Chem.*, 1997, **532**, 261.

31 (*a*) J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327 Based on our experimental data, we cannot rule out a transient dearomatization of the imidazolium heterocycle and nitrogen coordination to the metal center as an initial process for carbene metallation. Heteroatom-assisted C–H bond activation is well-known, see for examples; (*b*) A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403; (*c*) M. Albrecht and G. van Koten, *Angew. Chem. Int. Ed.*, 2001, **40**, 3750; (*d*) V. V. Dunina and O. N. Gorunova, *Russ. Chem. Rev.*, 2004, **73**, 309.

32 (*a*) D. L. Davies, S. M. A. Donald and S. A. Macgregor, *J. Am. Chem. Soc.*, 2005, **127**, 13754; (*b*) M. Albrecht, in *Palladacycles*, ed. J. Dupont and M. Pfeffer, Wiley-VCH, Weinheim, 2008, p.13.

33 The ligand precursor **9** was prepared by quaternizing a 1:1 mixture of N-isopropyl imidazole and the imidazole **1b** with CH_2I_2. This reaction produced, according to NMR integration, a mixture of the two homocoupled salts and the dissymmetric diimidazolium salt **9** in the statistically expected 1:1:2 ratio. After crystallization from MeOH, pure **9** was isolated in 25% yield, while a 1:1:1 mixture remained in solution.